High-Throughput Synthesis and Analysis for Searching New Permanent Magnet Materials

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High-Throughput Synthesis and Analysis for Searching New Permanent Magnet Materials

Gerhard Schneider, Dagmar Goll, Ralf Löffler, Roman Karimi
Aalen University, Materials Research Institute, Germany

- Motivation for searching new magnetic materials
- Selection of systems, prioritization
- High-throughput synthesis
- High-throughput analysis
Still great potential to find new materials with specific properties.

Need to develop High-Throughput methods.

Potential to discover new materials

Total: $7.7 \times 10^{25}$ systems
Motivation for the search of new magnetic phases

Key applications in energy conversion
- Generators
- Motors

Energy Product $(BH)_{\text{max}} / \text{kJ/m}^3$

Year

1900 1950 2000

$\text{Stahl}$ $\text{FePt}$

$\text{SmCo}_5$ $\text{Fe}_{65}\text{Co}_{35} + X$

$\text{AlNiCo}$ $\text{Sm}_2(\text{Co},\text{Cu},\text{Fe},\text{Zr})_{17}$ $\text{(Nd,Pr)}_2\text{Fe}_{14}\text{B}$

New microstructure
New phases

Situation: magnetic materials
Preconditions for permanent magnets

- Existence/stability of a phase with excellent intrinsic properties – \( \text{Fe}_{14}\text{Nd}_2\text{B} \)
  - Magnetocrystalline anisotropy \( H_A = 68 \text{ MA/m} \)
  - Saturation polarization \( J_s = 1.63 \text{ T} \)
  - Curie temperature \( T_C = 310 \text{ °C} \)
  - …

- Microstructure design – extrinsic properties
  - Avoid soft magnetic phases
  - Isolate aligned single crystal grains magnetically
  - Avoid nonmagnetic grains
Additional requirements for permanent magnets

**Temperature stability**
- Max. operating temperature of Fe-Nd-B: 180 °C to 200 °C

**Corrosion stability**
- Corrosion protection

**Raw material aspect**
- Content in earth crust:
  - Nd: 22 ppm
  - Dy: 4.3 ppm
  - Rare earth metals are expensive (97% China)
New Permanent Magnet Materials

max. energy product \((BH)_{\text{max}}\)

30% market share

Fe-Nd-B

55% market share

ferrite

Development goals:

- Magnetic performance \((B_R, H_C, T_C, \text{losses, ...})\)
- Lower material and processing costs, availability of raw materials
- Durability (aging, corrosion, mechanical properties, ...)

Situation: magnetic materials
Strategy High-Throughput experimentation

Corner stones for the search
(10^6 systems)

Priority setting
(10^3 systems)

High Throughput synthesis and analysis

Careful synthesis and analysis

Material development

processing, mass production
Corner stones

First selection of elements

- Ferromagnetic transition metals (TM)
  - Basis of ferromagnetism (high saturation polarization, high Curie temperature)
  - Economical

- Rare earth metals (RE)
  - Prerequisite for highest anisotropies
  - Mischmetals are cheaper than pure RE
  - Light RE are cheaper than heavy RE
  - La or Ce are available in larger amounts

- Additives
  - for stabilization of new phases or improving properties of known phases
  - non-toxic, non-radioactive
Estimation of the number of systems

- Selection of elements
  - TM: transition metals: Fe, Co, Ni, Mn; \( k = 4 \)
  - RE: rare earth metals: La, Ce, Y, Pr, Nd, Sm, Dy; \( j = 7 \)
  - Add: additives X; \( l = 41 \)

- RE systems
  - TM (unary), TM-RE (binary), TM-RE-X (ternary)

\[
\binom{TM}{k} \binom{Add}{l} \binom{RE}{j} = \frac{TM!}{(TM-k)!k!} \frac{Add!}{(Add-l)!l!} \frac{RE!}{(RE-j)!j!}
\]

- RE-free systems
  - TM (unary), TM-X (binary), TM1-TM2-X (ternary), TM-X1-X2 (ternary)

\[
\binom{TM}{k} \binom{Add}{l} = \frac{TM!}{(TM-k)!k!} \frac{Add!}{(Add-l)!l!}
\]
Estimation of the number of interesting systems

**RE-containing systems; log 10**
- Total: 443,156
-Unary: 4
-Binary: 28
-Ternary: 1,148
-Quaternary: 28,126
-Quinary: 413,854
-Total: 443,156

**RE-free systems; log 10**
- Total: 523,775
-Unary: 4
-Binary: 164
-Ternary: 3,526
-Quaternary: 47,724
-Quinary: 472,361
-Total: 523,775

Total number of systems: ~1,000,000
Known systems: ~1000
Ratio: ~1:1000

Area Northern Ireland
Area Europe
\[
\frac{1}{1000}
\]
New Phases and modification of known phases

- New Phases
  - New composition
  - New crystal structure
  - Examples:
    - Fe$_{14}$Nd$_2$B

- Known Phases
  - Homogeneity range
  - Additives
  - Examples:
    - (Fe,Co)$_{17}$Pr$_2$

- Microstructure optimization
Strategy High-Throughput experimentation

Corner stones for the search
(10^6 systems)

Priority setting
(10^3 systems)

High Throughput synthesis
and analysis

Careful synthesis
and analysis

Material development

processing, mass production
Prioritization

**Input data base**

<table>
<thead>
<tr>
<th>System</th>
<th>PI * KI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Y-C</td>
<td>5</td>
</tr>
<tr>
<td>Fe-Sm-C</td>
<td>6</td>
</tr>
<tr>
<td>Fe-Ce-C</td>
<td>9</td>
</tr>
<tr>
<td>Fe-Y-Ge</td>
<td>26</td>
</tr>
<tr>
<td>Fe-Y-Sn</td>
<td>28</td>
</tr>
<tr>
<td>Fe-Y-Mo</td>
<td>48</td>
</tr>
<tr>
<td>Fe-Sm-P</td>
<td>48</td>
</tr>
<tr>
<td>Fe-Y-Si</td>
<td>50</td>
</tr>
<tr>
<td>Fe-Sm-Mo</td>
<td>60</td>
</tr>
<tr>
<td>Fe-Nd-C</td>
<td>72</td>
</tr>
<tr>
<td>Fe-Y-P</td>
<td>72</td>
</tr>
</tbody>
</table>

**Priority setting (index)**
- Non toxic
- Cost efficient/ available
- Probability to form intermediate phases
- Physical principles
Search for new magnetic phases criteria for efficient synthesis

- High probability to receive numerous phases (e.g. stable and metastable)
  - Non-equilibrium states in binary and higher component systems
- Interest focused on TM-rich phases
- Small specimen
- Quick and easy process
- Grain size of new phases should be larger than 10 µm (due to analysis method)
The intermetallic phases form during isothermal annealing and during cooling.
Diffusion Couple Fe-Nd-B

Fe$_{14}$Nd$_2$B

Nd-rich eutectic

Fe

Fe$_4$Nd$_{1.1}$B$_4$
Diffusion Couple – Binary System Co-Sm

Compared to the phase diagram all phases are found in the diffusion couple.
High-throughput synthesis

Diffusion Couple – Binary System Fe-Nd

Figure 6.5: Bright field micrograph of an Fe-(Nd100) diffusion couple after a 1050°C heat treatment for 10 hours and 725°C for 30 days. For a better separation between the iron crucible (bottom), the Fe_{17}Nd_{5} phase (middle) and the Fe_{17}Nd_{2} phase (top) the specimen was etched with Nital.
High-throughput synthesis

Diffusion Couple – Ternary System Fe-(Nd-B)
Examples of Diffusion Couples – 400 in total
Efficient analysis: Search for new magnetic phases

- High-throughput
- Determination of the intrinsic magnetic properties
- Characterization of intrinsic properties in small crystals ($J_S$, $K_1$, $T_C$)
Efficient analysis: Search for new magnetic phases

- Correlative microscopy, quantitative microstructure analysis (QMA)

  Optical microscopy  Kerr microscopy  REM / EDX

Identification of different phases  Identification of magnetic phases  Determination of the chemical composition

Fe$_{86.5}$Nd$_{13.5}$ (φ)  Fe$_{78.4}$Nd$_{21.6}$ (η)
Domain pattern – large amount of phase
Domain pattern – small amount of phase
Ternary Fe-Pr-Mn-System

Photomicrograph of an unknown crystal surrounded by the 6/13/1 phase.

Optical micrograph in polarized light of the unknown crystal with uniaxial domain structure.
Diffusion Couple Fe-(Pr90-Na10)
Heat Treated at 1050 °C / 10h

Optical micrograph of the 17/2 phase and the eutectic.

Optical micrograph in polarized light of the A₁ phase with domain pattern.
Kerr effect using the example of Nd$_2$Fe$_{14}$B

- Linearly polarized light
- Magnetic field rotates plane of polarization ($R_{\text{tot}} = R_N + R_K$)
- Visualization of domains by analysator
- Domain contrast depending on magnetization

Bright field image, 200x
Kerr image, 200x
Domain pattern for uniaxial anisotropy (Nd$_2$Fe$_{14}$B)

Minimization stray field energy by reversed spikes

Stray field energy

3D-model

High-throughput analysis

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High-throughput analysis

Relationship between domain pattern and intrinsic magnetic properties

Domain contrast
- Saturation polarisation $J_s$

Domain width
- Domain wall energy $K_1$

Anisotropy field

Curie temperature

Fe$_{14}$Nd$_2$B $K_1 \sim 4.6$ MJ/m$^3$

Fe$_{14}$Y$_2$B $K_1 \sim 2.0$ MJ/m$^3$
High-throughput analysis

Saturation polarization $J_S$ from domain contrast

![Graph showing saturation polarization $J_S$ vs. domain contrast $K_{256}$ for various materials including Nd$_2$Fe$_{14}$B, Pr$_2$Fe$_{14}$B, Y$_2$Fe$_{14}$B, Ce$_2$Fe$_{14}$B, and BaFe$_{12}$O$_{19}$.](image)

Materials:
- Nd$_2$Fe$_{14}$B
- Pr$_2$Fe$_{14}$B
- Y$_2$Fe$_{14}$B
- Ce$_2$Fe$_{14}$B
- BaFe$_{12}$O$_{19}$

Reference samples for high-throughput analysis.
Anisotropy constant $K_1$ from domain width

- Different models for determination of $K_1$

<table>
<thead>
<tr>
<th>Domain pattern</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>stripe domain</td>
<td>$D_m = (\gamma L/1.7M_s^2)^{1/2}$</td>
<td>[Kit46] C. Kittel, Phys. Rev. 70, 965 (1946)</td>
</tr>
<tr>
<td>for grain thickness &lt; 10 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>stripe domain,</td>
<td>$D_m = 0.395(\gamma^*/M_s^2)^{1/3}L^{2/3}$</td>
<td>[Szy73] R. Szymczak, Acta Phys. Pol. A 43, 571 (1973)</td>
</tr>
<tr>
<td>for grain thickness &gt; 10 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>closure domain,</td>
<td>$D_s = \beta 4\pi\gamma/M_s^2$</td>
<td>[Bod77] R. Bodenberger, A. Hubert, Phys. Stat. Sol. (a) 44, K7-K11 (1977)</td>
</tr>
<tr>
<td>for grain thickness &gt; 80 µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Wall energy $\gamma = 4(AK_1)^{1/2}$, with exchange constant $A \approx 1*10^{-11}$ J/m

- For identical grain thickness phases with larger magnetocrystalline anisotropy show a larger domain width compared to phases with smaller anisotropy constant.
Anisotropy constant $K_1$ from domain width

$$D_s = \beta 4\pi y/M_s^2 \quad \text{[Bod77]} \quad (\beta = 0.31)$$

Kerr images, 1000x, oil pole
Anisotropy constant $K_1$ from domain width

$$D_m = 2.01 \pm 0.13$$
$$L = 30.49 \pm 0.54$$

$$D_m = 4.72 \pm 0.54$$
$$L = 109.14 \pm 1.09$$

$$D_m = 0.395\left(\gamma\mu^*/M_S^2\right)^{1/3}L^{2/3}$$ [Szy73]

Average grain thickness: $L$ [$\mu$m]
Average domain width: $D_m$ [$\mu$m]

Kerr image, 500x und 1000x oil pole
High-throughput analysis

Example \((Y_{1-x}Nd_x)_2Fe_{14}B\) (\(x = 0..1\))

\[
\begin{align*}
Y_2Fe_{14}B & \quad J_S = 1,38 T \\
Y_{1.7}Nd_{0.3}Fe_{14}B & \quad K_1 = 1,06 MJ/m^3 \\
Y_{1.0}Nd_{1.0}Fe_{14}B & \quad J_S = 1,61 T \\
Y_{0.3}Nd_{1.7}Fe_{14}B & \quad K_1 = 4,3 MJ/m^3 \\
Nd_2Fe_{14}B & \quad J_S, K_1, T_C
\end{align*}
\]

Behavior of \(J_S\) and \(K_1\) for RE mixtures

\[
\begin{array}{c}
\text{rule of mixture not valid} \\
\text{rule of mixture}
\end{array}
\]

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Example \((Y_{1-x}Nd_x)_{2}Fe_{14}B\) \(x = 0..1\)

- \(J_s\) and \(K_1\) as function of ratio \(Y:Nd\)

Estimation saturation polarization \(J_s\) based on measured domain contrast

Estimation anisotropy constant \(K_1\) based on measured domain surface width

High-throughput analysis
Search for new permanent magnetic materials

- High Throughput synthesis and analysis methods established
- Search in about 400 different systems completed
- Existence of phases in TM rich corner documented, some interesting candidates identified
- Still some work to be done!
  - Support by first principle approaches needed
    - Crystal structures, chemical composition
    - Thermodynamic stabilities
    - Magnetic properties
  - Collaboration with Peter Gumbsch and Ralf Drautz

Modeling tools still to be developed

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Fe\textsubscript{17}Sm\textsubscript{2}</th>
<th>Fe\textsubscript{3}Sm</th>
<th>Fe\textsubscript{3}Sm</th>
<th>Fe\textsubscript{12}Sm</th>
<th>Fe\textsubscript{20}Sm\textsubscript{3}</th>
<th>Fe\textsubscript{14}Sm\textsubscript{b}</th>
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<tbody>
<tr>
<td>Fe-Sm-Mg</td>
<td>$\times$</td>
<td>$\checkmark$ strong</td>
<td>$\checkmark$ weak</td>
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<tr>
<td>Fe-Sm-Ti</td>
<td>$\times$</td>
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<td>$\checkmark$ weak</td>
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<td>$\checkmark$ strong</td>
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<tr>
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<td>$\checkmark$ weak</td>
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<td></td>
<td>$\checkmark$ strong</td>
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<tr>
<td>Fe-Sm-Cr</td>
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<td>$\checkmark$ weak</td>
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<tr>
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<td>$\checkmark$ weak</td>
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<td>$\checkmark$ strong</td>
<td>$\checkmark$ weak</td>
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</tr>
<tr>
<td>Fe-Sm-Ni</td>
<td>$\times$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\checkmark$ strong</td>
</tr>
<tr>
<td>Fe-Sm-Cu</td>
<td>$\times$</td>
<td></td>
<td></td>
<td></td>
<td>$\checkmark$ strong</td>
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<tr>
<td>Fe-Sm-Zr</td>
<td>$\times$</td>
<td>$\checkmark$ strong</td>
<td>$\checkmark$ weak</td>
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<td></td>
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<tr>
<td>Fe-Sm-Nb</td>
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<td>$\checkmark$ strong</td>
<td>$\checkmark$ weak</td>
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<td></td>
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<tr>
<td>Fe-Sm-Mo</td>
<td>$\times$</td>
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<td>$\checkmark$ weak</td>
<td>missing</td>
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<td></td>
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<tr>
<td>Fe-Sm-In</td>
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<td>$\checkmark$ strong</td>
<td>$\checkmark$ weak</td>
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<tr>
<td>Fe-Sm-Sn</td>
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<td>$\checkmark$ weak</td>
<td></td>
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<td></td>
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<tr>
<td>Fe-Sm-Sb</td>
<td>$\checkmark$ weak</td>
<td>$\checkmark$ weak</td>
<td></td>
<td>$\times$</td>
<td></td>
<td></td>
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<tr>
<td>Fe-Sm-W</td>
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<tr>
<td>Fe-Sm-Pb</td>
<td>$\times$</td>
<td></td>
<td>$\times$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
New phase found
Phase in larger amount synthesized and analyzed
Development of processing to realize microstructure
Mass production

“This could be the discovery of the century. Depending of course, on how far down it goes.”
Acknowledgements

- Bundesministerium für Bildung und Forschung
- Robert Bosch GmbH
- Magnetfabrik Bonn
- Fraunhofer-Institut für Werkstoffmechanik
- Max-Planck-Institut für Intelligente Systeme
Backup
Search for new magnetic phases – efficient synthesis

- High probability to receive numerous phases
- Non-equilibrium states in binary and higher component systems
- Interest focused on TM-rich phases
- Small specimen

The intermetallic phases form during isothermal annealing and during cooling.
Heterogeneous non-equilibrium states
High-throughput analysis

**Anisotropy constant $K_1$ from domain width**

- Dependence of domain pattern on grain thickness

Kerr microscope image
Nd$_2$Fe$_{14}$B, 1000x, oil pole  

Kerr microscope image
Nd$_2$Fe$_{14}$B, 100x
Diffusion Couple – Binary System Fe-Nd

According to the phase diagram all phases are found.
Saturation polarization $J_S$ from domain contrast

<table>
<thead>
<tr>
<th>Literature values</th>
<th>$J_S$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td>$\sim$0.3</td>
</tr>
<tr>
<td>Ce$<em>2$Fe$</em>{14}$B</td>
<td>1.17</td>
</tr>
<tr>
<td>Y$<em>2$Fe$</em>{14}$B</td>
<td>1.38</td>
</tr>
<tr>
<td>Pr$<em>2$Fe$</em>{14}$B</td>
<td>1.56</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>1.61</td>
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</table>